

Article

Pyrolysis of *Persea americana* Pruning Residues: Kinetic and Thermodynamic Analyses

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Abstract

The transition towards a circular bioeconomy drives the search for sustainable valorization routes for agricultural waste streams. In this context, lignocellulosic residues from avocado tree prunings (*Persea americana* Mill.), with a reported high extractives content, represent a promising resource for pyrolytic valorization; however, their thermal behavior remains scarcely studied. This work characterized the chemical composition of whole branches (including bark) by FTIR and evaluated thermal degradation by thermogravimetric analysis (TGA) at five heating rates (10–30 °C/min) in an inert atmosphere. Kinetic analysis of the TGA data employed Friedman, FWO, KAS, Coats–Redfern, and Kissinger models. The Avrami model determined a reaction order of $n \approx 0.28$. Among the methods, Coats–Redfern, applied with this n , provided the most consistent description, achieving the best average fit ($R^2 \approx 0.9878$) and the narrowest range of pre-exponential factors (10^{12} – 10^{16} s^{−1}). The Friedman model showed greater dispersion (10^{12} – 10^{22} s^{−1}). Average activation energies ranged from 185 to 210 kJ/mol (Kissinger: 171.3 kJ/mol). The thermodynamic parameters confirmed a non-spontaneous, endothermic process ($\Delta H = 166.4$ – 205.9 kJ/mol; $\Delta G = 178.8$ – 179.8 kJ/mol). The entropy change (ΔS from -33.8 to 194.1 J/mol·K) reflects the complex solid-to-volatiles transition during pyrolysis. This study establishes a tailored kinetic framework for avocado branch pyrolysis, providing a reliable kinetic description for this biomass and identifying the Avrami–Coats–Redfern method as the most suitable for its accurate modeling.

Keywords: avocado branches; kinetic analysis; TGA-DTG; pyrolysis; thermodynamic parameters



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1. Introduction

Agroindustries in Mexico produce significant volumes of lignocellulosic residues, but valorizations of this material are currently limited or null, especially for prunings from fruit trees. Inadequate disposal of these residues raises operating costs and contributes to environmental contamination [1,2]. Among these residues, those derived from avocado cultivation (*Persea americana* Mill.) stand out due to their volume and economic importance, since Mexico is the world's largest producer with over 268,000 hectares planted, according to Mexico's *Servicio de Información Agroalimentaria y Pesquera* (SIAP) [3]. Regular prunings generate lignocellulosic biomass that constitutes a potential resource for evaluating thermochemical processes, such as pyrolysis, with the goal of obtaining biocarbon, biooils, and combustible gases [4,5].

Previous studies have focused on byproducts of *P. americana* like seeds [6], but its woody residues present differentiated chemical and structural compositions characterized by a higher proportion of lignocellulose and lower extractive content. These properties suggest a more stable, homogeneous thermochemical behavior that makes them especially adequate for obtaining high-quality biochar, though this constitutes only one possible route of valorization, so it is necessary to explore other alternatives for products derived from thermochemical transformation.

Despite pyrolysis' high potential for valorizing lignocellulosic residues, implementation on an industrial scale faces technical and economic limitations, such as low product yield and high operating costs. These restrictions underscore the need to optimize both the design of reactors and their operating conditions, based on reliable experimental data to improve process efficiency [7–9]. Other significant challenges for industrial scaling are the intrinsic variability of the physicochemical properties of biomass and the lack of standardized experimental procedures.

In this context, thermogravimetric analysis (TGA) complemented by its derivative (DTG), constitutes a fundamental tool for characterizing the thermal stability of biomass, identifying the stages of degradation, and determining critical process temperatures [10]. Data obtained through TGA–DTG make it possible to estimate the essential kinetic parameters of thermal degradation; namely, activation energy (E_a), which represents the energy barrier of the reaction, the pre-exponential factor (A) that reflects the frequency of molecular collisions with an adequate orientation, and the reaction order (n), which describes the relation between the reaction velocity and degree of conversion, thus mirroring the complexity of the entire process [4,11,12]. Although the experimental conditions for TGA do not reproduce the heating rates or thermal regimens of industrial processes, results constitute an essential tool for understanding thermal stability, the stages of degradation, and the kinetic dynamics of lignocellulosic materials. This experimental information also supports the application of kinetic focuses for analyzing and modeling thermal degradation processes.

Researchers in this field have developed iso-conversional kinetic methods, like the Friedman, Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) approaches, that do not require assuming a specific reaction model [13], as well as non-iso-conversional methods (Kissinger, Coats–Redfern), which do assume a defined reaction model and are recognized as providing reliable estimates of kinetic parameters [14]. Avrami's model is widely used to describe the reaction kinetics of heterogeneous materials [15]. Our work team has applied it recently in thermal analyses of woody biomass from *Ceiba aesculifolia* [12]. It is important to note, finally, that the Coats–Redfern method has shown reliable adjustment with distinct biomasses, including woody ones [16–18].

Thermodynamic analysis complements kinetic characterizations by providing information on the energy and viability aspects of the process. Parameters like activation enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) allow us to evaluate the energy efficiency

and spontaneity of reactions [19]. Integrating this with kinetic data, as recommended, ensures a more complete characterization of the thermochemical behavior of biomass [20].

In light of its reported composition, which includes relatively high extractives content, a detailed investigation of the pyrolysis kinetics of this specific biomass is warranted. The present study was conceived to characterize the woody residues of *P. americana* by FT-IR spectroscopy to identify the predominant functional groups and evaluate their thermal behavior during pyrolysis using TGA and DTG at five heating rates. These data were used to determine kinetic and thermodynamic parameters in order to provide rigorous technical information that supports the valorization of this residual biomass as a renewable resource in thermochemical processes.

To establish the technical foundation for this valorization pathway, this study focuses on *P. americana* pruning residues—an abundant yet under-characterized biomass whose reported composition, including a relatively high extractives content, may distinctly influence its thermal decomposition. Consequently, this work aims to characterize the biomass's functional groups via FT-IR spectroscopy, analyze its thermal degradation behavior using TGA/DTG at multiple heating rates, and determine the associated kinetic and thermodynamic parameters. This integrated analysis provides the rigorous data necessary to support the efficient valorization of this residual biomass as a renewable resource in thermochemical processes.

2. Materials and Methods

The sample materials were gathered after pruning in six orchards in the municipality of Salvador Escalante, Michoacán, Mexico. During collection, the branches—the principal fraction of interest—were separated and the leaves discarded. Branches were analyzed with their bark to reflect the typical composition of pruning waste. The selected material was transported to the laboratory for pre-drying, followed by grinding in a model K20F mill (Micron S.A. de C.V., Mexico) and sieving through a ROTAP device (model RX-29, W.S. Tyler, U.S.) equipped with a standard ASTM No. 40 mesh (425 μm). The physicochemical properties of the woody fraction of prunings of *P. americana* have been determined previously [21]. Table 1 shows the results of that characterization.

Table 1. Reference data for avocado pruning branches from a previous study by Soria-González et al. [21], including higher heating value, proximate analysis, elemental composition, and basic chemical composition.

Parameter	Units	Avocado Branches
Higher Heating Value (HHV)	MJ/kg	19.7
Proximate Analysis (wt.%, dry basis)		
Ash	%	1.2
Volatile matter	%	83.9
Fixed carbon	%	14.9
Ultimate Analysis (wt.%, dry basis)		
Carbon	%	47.0
Hydrogen	%	6.0
Oxygen	%	46.3
Nitrogen	%	0.8
Sulfur	%	<0.01
Basic Chemical Analysis		
Cellulose	%	46.8
Hemicellulose	%	20.6
Lignin	%	14.5
Extractives (by difference)	%	17.0

2.1. Fourier Transform Infrared Spectroscopy

The functional characterization was conducted by Fourier transform infrared spectroscopy in transmission mode, using a Spectrum 400 spectrometer (PerkinElmer, Waltham, MA, USA). Samples of *P. americana* were dried at 105 °C for 24 h, pulverized, and mixed with potassium bromide (KBr) to form pellets. Spectra were recorded in the interval of 4000–500 cm^{−1}, at a resolution of 4 cm^{−1} and 16 scans per sample.

2.2. Thermal, Kinetic, and Thermodynamic Analyses

2.2.1. Thermal Analysis (TGA–DTG)

The ground, sieved samples of biomass were dried to a constant weight at 105 °C, then stored in hermetic recipients. TGA was performed on an STA 6000 analyzer (PerkinElmer Inc., USA). Samples (30 ± 5 mg of dried material) were analyzed in triplicate in a 99.99% N₂ atmosphere. The sample mass used here exceeds the amount typically recommended to minimize the influence of transport phenomena on the reaction rate. It was chosen to ensure a representative signal, which leads to the determination of apparent kinetic parameters that represent the effective global behavior of the system. The flow rate was 30 mL/min, adjustable according to the heating velocity. The thermal program consisted in heating from room temperature (~25 °C) to 900 °C with a final isotherm of 10 min, at five speeds: 10, 15, 20, 25, and 30 °C/min (10–30 K/min). The thermogravimetric data (TGA) were processed with OriginPro (trial version) software (OriginLab, Northampton, MA, USA) to generate the decomposition data of the biomass and its derivatives (DTG) and then represent them in graphs.

2.2.2. Kinetic Analysis

Kinetic parameters were determined on the basis of the TGA–DTG results using, initially, the Friedman, Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), and Coats–Redfern iso-conversional methods, as well as Kissinger’s non-iso-conversional approach, adjusted to the experimental data obtained at the five heating velocities (10–30 °C/min). The aim was to simultaneously estimate E_a and A under a defined reaction model. Later, Avrami’s model was applied to describe the reaction order (n). Graphs were generated in OriginPro, respecting the theoretical foundations and equations reported in the literature, as described in detail below.

To estimate the kinetic parameters, conversion (α) was determined on the basis of mass loss during pyrolysis, according to Equation (1) [22]:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (1)$$

where m_0 is the initial weight loss from the biomass, m_t represents the weight loss at a specific temperature, and m_f is the final weight of the biomass.

The kinetic models employed to determine these parameters are based on the general equation for the reaction velocity reported in the literature [22], as shown in Equation (2):

$$\frac{d\alpha}{dt} = A \cdot e^{\left(\frac{-E_a}{RT}\right)} \cdot f(\alpha) \quad (2)$$

where $d\alpha/dt$ is the change in the degree of advance with respect to time, A is the pre-exponential factor, (s^{−1}), E_a is the activation energy (kJ/mol), R is the universal constant of the ideal gases, T is the absolute temperature in Kelvin (K), and $f(\alpha)$ represents the reaction model of the pyrolysis process.

Because the thermal decomposition of lignocellulosic biomass involves multiple reactions, it entails a multistep process. Vyazovkin et al. [13], however, hold that in a condensed

phase process, the kinetics of multiple steps can approach with precision those of a one-step process. The challenge involved in identifying the reaction models intensifies when adjustment is made on experimental data obtained from a non-isothermal assay at a single heating velocity, β . Nonetheless, when the temperature varies linearly with time under non-isothermal conditions, Equation (3) can be applied:

$$\beta = \frac{dT}{dt} \quad (3)$$

Using this ratio, Friedman's differential method [23]—described in Equation (4)—is initially based on Arrhenius' modified equation. In this method, the dependence of time on the degree of conversion ($d\alpha/dt$) from Equation (2) is replaced by the temperature/time ratio (dT/dt) from Equation (3). This allows for the derivation of an expression that uses different β values [22,23]:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (4)$$

To apply Friedman's method, it is assumed that the function of the reaction mechanism $f(\alpha)$ remains constant for a fixed value of α . This approach did not require a predefined reaction model to calculate E_a from the data obtained by thermogravimetry (TGA-DTG) at the five heating rates. The general equation of Friedman's method is derived by simplifying and applying the natural logarithm to both sides of Equation (4) to generate Equation (5) [22,23]:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (5)$$

Kissinger's method [24] is a kinetic technique used to estimate E_a from the temperature that corresponds to the maximum reaction rate, or maximum peak, found in a thermogravimetric analysis at distinct heating rates. This focus does not require previous knowledge of the reaction mechanism, so it is especially useful for studying materials with complex structures. Estimates of E_a depend on the mathematical relation expressed in Equation (6), which represents the characteristic formulation of this method [22,24]. E_a is calculated from the slope of the straight line in the graph, which is equal to E_a/R .

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (6)$$

FWO is a widely used iso-conversional method, one of the first traditional integral approaches. Equation (7) presents the mathematical expression that describes FWO [4,25].

$$\ln(\beta) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - 5.331 - 1.052 \frac{E_a}{RT} \quad (7)$$

where $g(\alpha)$ is obtained by introducing the integral function of $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ into Equation (5) to generate Equation (8), shown below [4,25]:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{\left(\frac{-E_a}{RT}\right)} dT \quad (8)$$

KAS is another iso-conversional method. It is a function of the integral of temperature expressed in Equation (9) [4,26]:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \left(\frac{E_a}{RT}\right) \quad (9)$$

Avrami's kinetic model [15] is used to determine the reaction order (n). The general formulation of this model was reported previously by Alvarado-Flores et al. [12]. It is expressed in Equation (10):

$$(1 - \alpha) = \exp \left[- \left(\frac{k(T)}{\beta} \right)^n \right] \quad (10)$$

where $k(T)$ is the temperature-dependent velocity constant and n is the reaction order. Equation (11) is obtained by applying double natural logarithms to the original equation and then performing an algebraic reorganization. Equation (11) is used experimentally to determine the parameter n , which corresponds to the reaction order:

$$\ln[-\ln(1 - \alpha)] = \ln A - \frac{E_a}{RT} + n \ln \beta \quad (11)$$

Values of n are obtained by means of the graphic representation of $\ln[-\ln(1 - \alpha)]$ against $\ln \beta$ at a constant temperature.

Avrami's model makes it possible to estimate the reaction order, n , which was used as the basis for applying Coats–Redfern's integral method. This combination allowed us to estimate the dominant kinetic mechanism in the interval analyzed. In our work, we utilized the integral function $g(\alpha)$, shown in Equation (12), which corresponds to the reaction order calculated previously by adapting the normalized Coats–Redfern equation [27]:

$$\ln \left(\frac{g(\alpha)}{T^2} \right) = \ln \left(\frac{AR}{\beta E_a} \right) - \frac{E_a}{RT} \quad (12)$$

where $g(\alpha)$ represents the integral function of the assumed kinetic model.

The experimental data obtained at five heating rates (10, 15, 20, 25, 30 °C/min) are represented graphically as $\ln(g(\alpha)\beta/T^2)$ against $1000/T$. This procedure allowed us to evaluate the concordance of the model with the thermal behavior of the biomass and generate robust estimates of the kinetic parameters. To compare these findings to distinct β values in the thermogravimetric assays, the method was applied assuming a regimen of linear heating that explicitly incorporated the term β into the equation to normalize its effect and allow direct comparisons among different experiments. A model of order n was also assumed in accordance with earlier studies of woody biomass that have reported an adequate adjustment using this approach [17]. In addition, the integral function that corresponds to a model of the reaction order, n , was utilized with the expression in Equation (13):

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n}, n \neq 1 \quad (13)$$

where n corresponds to the estimated value achieved with Avrami's model.

The decision to use the experimental value of the reaction order (n), derived from the Avrami model, made it possible to avoid assigning an arbitrary theoretical order and to maintain consistency between the adjusted parameters and the available experimental information. The methodological strategy included the parallel application of iso-conversional methods (FWO, KAS, and Friedman) and non-iso-conversional methods (Kissinger), together with the Coats–Redfern integral method, in accordance with the recommendations of the ICTAC Kinetics Committee, which suggest combining and comparing different approaches for the kinetic analysis of complex, multistep systems [20]. This integrated approach provides a solid basis for determining global and conversion-dependent kinetic parameters, avoiding dependence on a single model or prior assumptions.

Table 2 presents a summary of the kinetic methods applied and highlights their key features, including type of method, main assumptions, and the variables utilized to graph

the data required to determine the kinetic parameters. It also displays an overview of the methods selected to analyze the thermal degradation of *P. americana*, described above.

Table 2. Kinetic methods applied in this study (*P. americana*).

Method	Method	Main Assumptions	Key Notes	Plotting Variables	Refs.
Friedman	Differential isoconversional (model-free)	No predefined reaction model; $f(\alpha)$ assumed constant for a fixed α .	Determines E_a point-by-point from $\ln(d\alpha/dt)$ vs. $1/T$. Sensitive to experimental noise; useful for detecting E_a variability with conversion.	$\ln(d\alpha/dt)$ vs. $1/T$	[22,23]
Flynn–Wall–Ozawa	Integral isoconversional (model-free)	No kinetic model required; multiple heating rates necessary.	Uses Doyle approximation to estimate E_a across α . Robust for multistep systems but relies on an integral approximation.	$\ln(\beta)$ vs. $1/T$	[5,22,25]
Kissinger–Akahira–Sunose	Integral isoconversional (model-free)	No kinetic model required; multiple heating rates used.	Based on a linear temperature-integral approximation; provides slightly more accurate E_a estimates than FWO. Does not directly yield A unless combined with a reaction model or complementary analysis.	$\ln(\beta/T^2)$ vs. $1/T$	[5,22,26]
Kissinger (classical)	Non-isoconversional (model-fitting, single-peak)	Assumes a dominant single step; uses peak temperature (T_p) of maximum reaction rate.	Quick estimation of E_a from T_p dependence on heating rate. Does not provide E_a or A as a function of conversion; suitable for preliminary assessment.	$\ln(\beta/T_p^2)$ vs. $1/T_p$	[12,24]
Avrami	Model-fitting (mechanism/order)	Assumes an order n characteristic of the system; used to estimate apparent reaction order.	Estimates reaction order n . Useful to capture non-integer kinetics and heterogeneity in biomass pyrolysis; derived n can inform model-fitting methods.	$\ln[-\ln(1-\alpha)]$ vs. $\ln(\beta)$	[12,15]
Coats–Redfern	Integral model-fitting (requires $g(\alpha)$)	Although the method requires an assumed $g(\alpha)$, in this study it was defined using the Avrami reaction order (n).	Provides simultaneous estimates of E_a and A under a defined reaction model. Applied here using the fractional-order $g(\alpha)$ to compare first-order vs. fractional behavior.	$\ln[g(\alpha)/T^2]$ vs. $1/T$	[16–18,27]

2.2.3. Estimates of the Thermodynamic Parameters

To estimate the thermodynamic parameters associated with pyrolysis, we applied transition state theory (Eyring’s theory), which makes it possible to calculate changes in enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) based on kinetic parameters obtained previously (E_a , A). This procedure is widely accepted in thermoanalytic studies of biomass [19,20]. Equations (14)–(16) are the mathematical expressions employed to perform this calculation:

$$\Delta H = E_a - RT \quad (14)$$

$$\Delta G = E_a + RT_p * \ln\left(\frac{K_B T_p}{hA}\right) \quad (15)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_p} \quad (16)$$

where T_p is the temperature at the maximum velocity of mass loss, K_B is Boltzman’s constant ($1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}$), T_p is the temperature, and h is Plank’s constant ($6.626 \times 10^{-34} \text{ Js}$).

3. Results and Discussion

3.1. Fourier Transform Infrared (FT-IR) Spectroscopy

Figure 1 displays the FT-IR spectra with absorption bands assigned to the functional groups typical of lignocellulosic biomass.

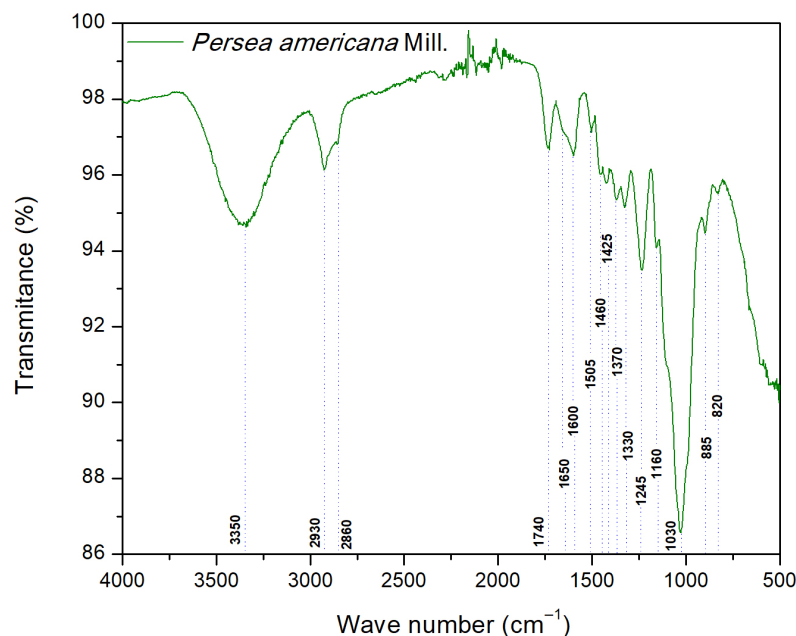


Figure 1. Fourier transform infrared spectra of *Persea americana*.

The FTIR spectra of branches of *P. americana* showed ample vibration coupled with medium-intensity signals in the 3700–2800 cm^{-1} region that evidence the presence of predominant O-H and C-H bonds. The broad, intense absorption identified around 3350 cm^{-1} corresponds to O-H stretching vibrations of hydroxyl groups in the alcohols, and carboxylic acids present in cellulose [28,29]. The 2930–2860 cm^{-1} region registered vibrations associated with C-H stretching of methyl and methylene groups [30,31], while around 2860 cm^{-1} a signal attributable to C-H vibrations of methylene groups was observed, which is particularly interesting, since in recent comparative studies consulted, this band was not reported for other woods such as *Ceiba aesculifolia* or *Prosopis laevigata* [12,32]. This absorption could be partly related to the content of certain extractable components in the biomass; relatively high levels of extractables (~17%) have been reported for *P. americana* [21] and other studies have identified compounds such as fatty acids (e.g., oleic and palmitic) in branches or other parts of the tree [33,34]. Nevertheless, given that this study did not include the characterization of these fractions, the possible link between the extractables and the band at 2860 cm^{-1} should be understood solely as an interpretation based on comparison with the recent references indicated above. The literature indicates that, in some biomass systems, lipid components can affect the onset of thermal degradation and the distribution of products in the early stages of the process [35].

The middle region of the spectra (1800–1300 cm^{-1}) showed predominantly well-defined absorptions of high and moderate-to-low intensity that allowed us to distinguish specific contributions of lignin, hemicellulose, and cellulose. The vibration at 1740 cm^{-1} was linked to C=O stretching of carbonyl groups, mainly associated with hemicellulose, reported between 1750 and 1720 cm^{-1} [28,29]. At 1650 cm^{-1} , a low-intensity signal was observed and attributed to conjugated C=O, absorbed O-H, and conjugated C-O that, like the dominant signal recorded around 1600 cm^{-1} , were associated with aromatic structures common in lignin [28]. The low-intensity absorptions at 1505 and 1460 cm^{-1} correspond,

respectively, to skeletal aromatic vibrations of C=C of lignin and asymmetric deformations of -CH₃ and -CH₂ groups in hemicellulose and lignin [28,29,31].

At 1425 cm⁻¹, we identified vibrations attributed to flexion vibrations of the CH₂ group, associated primarily with structures in cellulose and lignin [29,31]. The absorptions at 1370 and 1330 cm⁻¹, clearly differentiated as individual vibrations, were attributed to flexion CH₂, symmetric C-H deformation (1370 cm⁻¹), and C-H deformation and flexion on the C-O-H plane (1330 cm⁻¹), mainly associated with cellulose and hemicellulose [28,29], but also related to lignin in the 1320–1316 cm⁻¹ zone [28,36].

Observations for the 1245–820 cm⁻¹ region showed well-resolved absorptions of variable intensity that allowed us to clearly identify contributions by hemicellulose (silane), cellulose, and lignin. The vibration at 1245 cm⁻¹ was related to C-H flexions and C-O stretching in cellulose, hemicellulose, and lignin [12,31,32], while the signal at 1160 cm⁻¹ was attributed to C-O-C stretching in pyranose rings and C-O stretching in cellulose and hemicellulose [29,31]. The strong vibration at 1030 cm⁻¹ was characteristic of lignin, associated with C-H and C-O deformations [29,37]. A low-intensity vibration at 885 cm⁻¹ was related to C-H vibrations in cellulose [29,31]. Finally, there was a vibration around 820 cm⁻¹. These two results were associated with vibrations outside the C-H plane of lignin [28].

The FTIR analysis of the branches of *P. americana* confirmed the presence of the typical functional groups of woody lignocellulosic biomass, associated with cellulose, hemicellulose, and lignin, findings that are consistent with those reported for other woody biomasses. A signal was also observed around 2860 cm⁻¹, which constitutes a distinguishing feature of this species according to the literature. This chemical particularity could impact the initial or intermediate stages of thermal degradation and the distribution of pyrolytic products, so it complements the interpretation of the results obtained through TGA-DTG and the kinetic and thermodynamic analyses.

3.2. Thermal, Kinetic, and Thermodynamic Analyses

3.2.1. Thermal Analysis (TGA–DTG)

Figure 2 presents the TGA–DTG curves obtained at the five heating rates. For graphical clarity, the temperatures are shown in °C, while absolute temperatures in Kelvin were used in the kinetic analysis. Observations showed a progressive reduction in mass as temperatures increased, with a more pronounced loss between 250 °C and 380 °C. As the heating rate increased, the curves shifted toward higher temperatures, while the final residual mass showed an almost constant trend with slight variations among the different rates. A detailed examination of the DTG curves indicates that the residue was slightly higher at the lowest rate compared to the highest. Two well-defined peaks were identified in the DTG curves, characteristic of the thermal degradation of lignocellulosic biomass. They correspond to distinct stages of the decomposition of the principal components. The first one, between 26 and 150 °C, intensified at 30 °C/min and was related to moisture loss and the release of volatiles.

The second peak, broader and more intense, extended from 180 to 430 °C with more accelerated degradation between 330 and 380 °C. It was attributed to the decomposition of hemicellulose, cellulose, and lignin. In addition to the shift of the principal peak toward higher temperatures as the velocity increased, we observed a rightward horizontal movement of the curves.

The maximum degradation temperature (T_p) (Figure 2) increased with the heating rate, reflecting a thermal shift characteristic of processes limited by heat transfer. This behavior, consistent with studies of similar lignocellulosic biomasses, is often attributed to the lower availability of time for reactions to occur at low temperatures, as this demands

higher temperatures to achieve an equivalent degradation [38]. The absence of widening of the DTG peaks suggests that the shifts respond mainly to thermokinetic phenomena that reflect a uniform thermal decomposition of the material with no evidence of fractions with differentiated behaviors. The overlap in the curves at 15 and 20 °C/min between 120 and 200 °C indicates that those thermal transformations had low dependence on the heating rate. This concurs with reports on similar lignocellulosic biomasses and reveals that the effects of β are more important in advanced stages of volatilization [38,39].

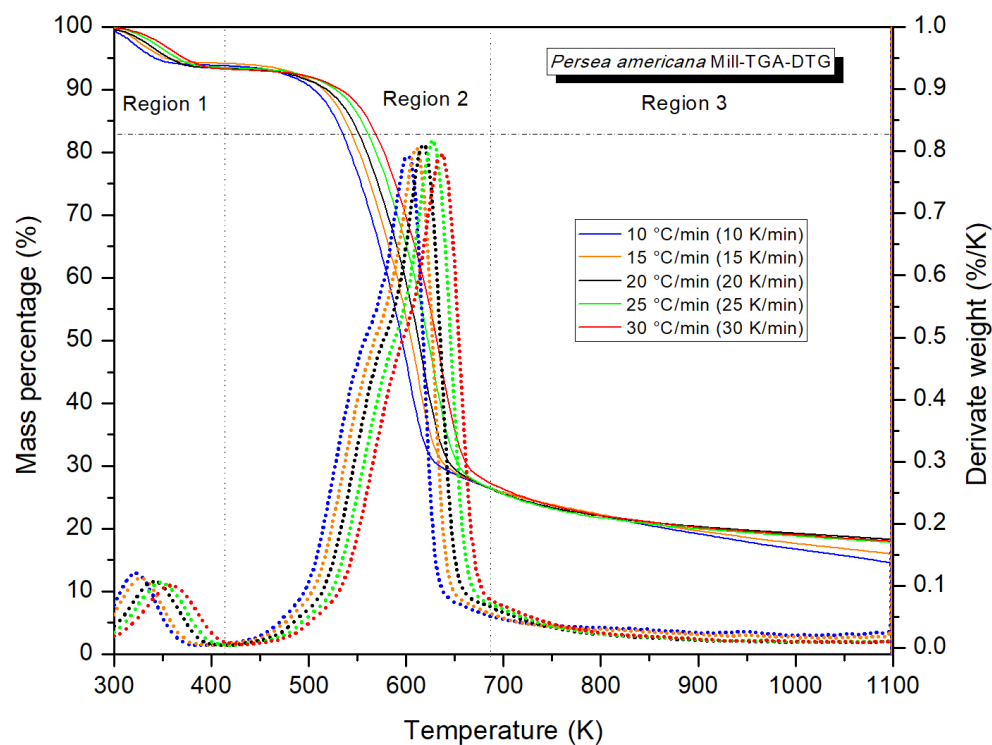


Figure 2. TGA–DTG curves of *Persea americana* under N₂ at different heating rates.

Figure 2 highlights three principal regions. Region 1 is characterized by a slight loss of mass, attributed mainly to the elimination of residual moisture and low-molecular-weight volatile compounds, including some extractables [40].

In region 2, the active phase of pyrolysis begins at around 200 °C and maintains a predominantly endothermic behavior up to 330–400 °C that corresponds to the decomposition of the structural components of the biomass [41]. Here, we observe the greatest mass loss, with a main peak that intensified between 315 and 360 °C and an inflexion in the DTG curve that shifted from 280 to 340 °C with increases in the heating rate. This reflects the active stage of pyrolysis. This behavior is related to the joint decomposition of hemicellulose, cellulose, and lignin, according to descriptions in the literature, where cellulose degrades predominantly between 250 and 380 °C, with a maximum near 345 °C, while lignin presents a wider range (200–500–527 °C) with a maximum around 400 °C [42–44]. In contrast to those reports, however, in the present study the greatest intensity of decomposition was determined for the interval 315–360 °C, indicating accelerated degradation of the structural components with intense molecular fragmentation. This stage, which is crucial for energy conversion, was characterized by the release of volatile compounds like condensable hydrocarbons, tars, and gases [45]. Kan et al. [35] pointed out that this is the range of greatest interest for examining the fundamental chemical mechanisms of the process. Osman et al. [46] added that the formation of unstable intermediates begins around 240 °C. Through dehydration and rupturing, they produce CO₂, H₂O, and CO.

Those authors affirm that demethylation occurs at temperatures $>300\text{ }^{\circ}\text{C}$ with CH_4 formation. This concurs with the observations in our work regarding the generation of volatile products and their contribution to syngas production.

Region 3 of the DTG curves shows a gradual degradation beginning at $400\text{ }^{\circ}\text{C}$, with less mass loss at high heating rates. This generates a relatively greater residual fraction and shows that part of the lignin does not decompose completely, so it fosters formation of carbonous residue. This tendency agrees with findings from earlier studies which state that the slow kinetics of lignin limit the release of volatiles and promote recombination reactions that generate carbon (char) with high superficial reactivity and notable thermal stability, associated with condensed aromatic networks [47,48]. Our work further identified tendencies that concur with those in Mishra & Mohanty [18], which suggest that lower heating rates foster the volatilization of organic compounds that could impact yields and the composition of biooil. Finally, this stage was characterized by condensation, dehydrogenation, and deoxygenation reactions that stabilized the char and strengthened its potential as a precursor of activated carbon [49].

The TGA–DTG analysis of the branches of *P. americana* evaluated at heating rates of 10, 15, 20, 25, and $30\text{ }^{\circ}\text{C}/\text{min}$ showed that active pyrolysis occurs primarily between 315 and $360\text{ }^{\circ}\text{C}$, the maximum decomposition peaks. At temperatures above $400\text{ }^{\circ}\text{C}$, degradation proceeds more slowly and fosters the formation of a stable carbonous residue. These results confirm the suitability of this biomass for thermochemical processes and the importance of controlling temperature and heating rate to optimize efficiency and the quality of the products obtained.

3.2.2. Kinetic Analysis

The kinetic analysis of *P. americana* was conducted using the thermoanalytic data, considering the conversion range $\alpha = 0.15\text{--}0.70$, which corresponds to the principal stage of thermal decomposition where greatest mass loss occurs due to degradation of the predominant structural components (Figure 3). It is important to mention that one of the parameters that allows us to consider the calculation of activation energy and the pre-exponential factor, is the correlation coefficient (R^2). In this research, we considered this parameter to be valid when it was above 0.95. In this sense, alpha (α) ranges lower than 0.15 and higher than 0.70 were not considered because the R^2 value was very low. This range was selected because it represents the “active stage” of pyrolysis, where biomass decomposition allows for more representative kinetic parameters to be obtained. The initial and final stages were excluded because they present less uniform kinetic phenomena, which could introduce variability in the adjustments. This selection is consistent with recent studies on lignocellulosic biomass, where the kinetic parameters are more stable and suitable for modeling within this conversion range [11].

Results of the Friedman, FWO, KAS, Coats–Redfern and Kissinger (Figure 3a–e) kinetic methods confirm the applicability of each model to the biomass of *P. americana* since they generated reliable estimates of the kinetic parameters without assuming any specific reaction mechanism. The Friedman, FWO, and KAS methods produced shifts in the curves as conversion increased, reflecting the multistage nature of thermal degradation and progressive variations in E_a associated with the decomposition of the structural components of the biomass [19,50]. The curves for the intermediate conversion intervals are grouped, show less variation in E_a but a relatively constant behavior during high conversions. The graph of Kissinger’s method supports the finding that the principal reaction occurred during a dominant step. This allowed us to estimate E_a reliably within the velocity ranges analyzed.

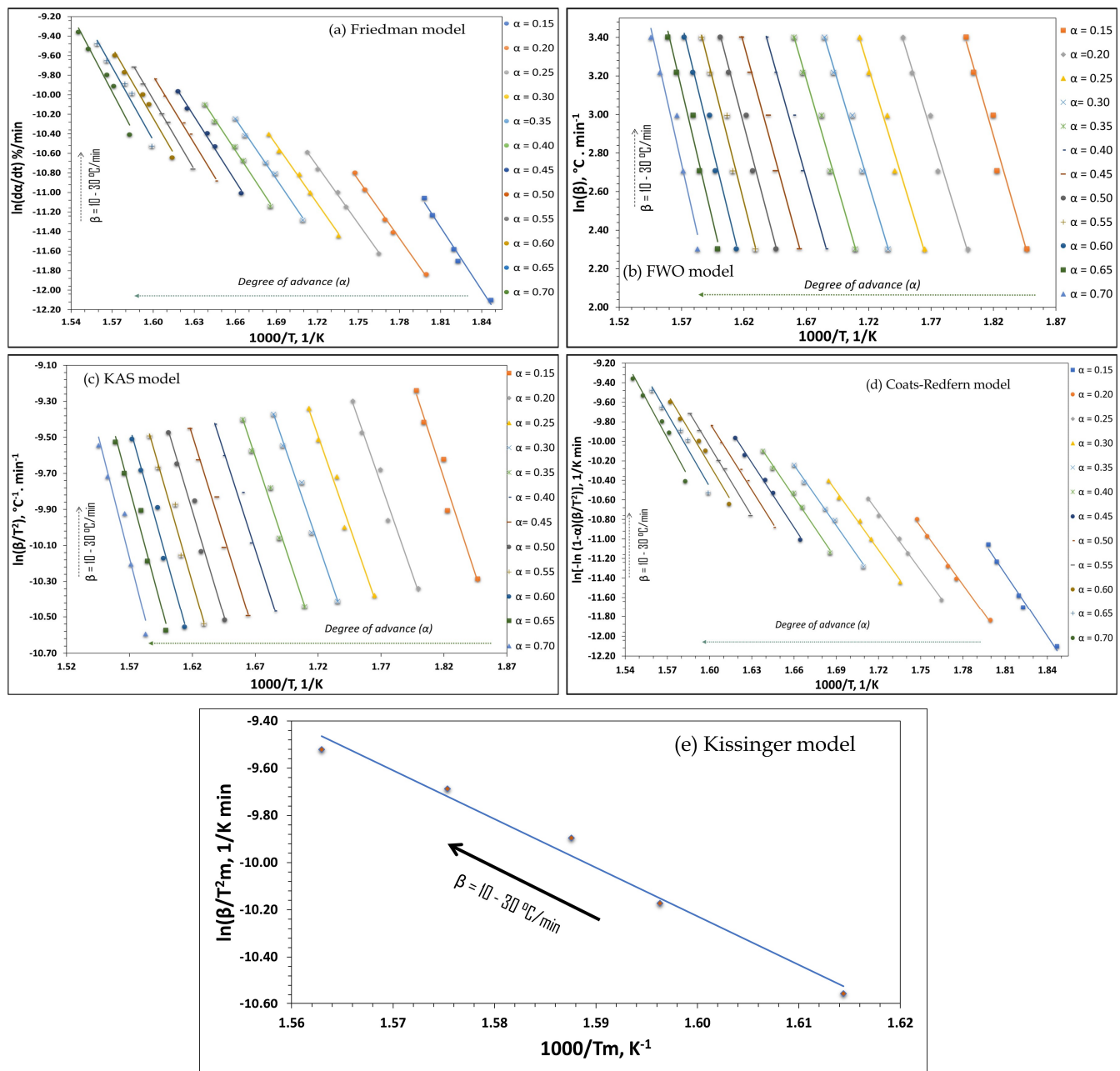


Figure 3. Linear fittings obtained from the applied kinetic methods: (a) Friedman, (b) Flynn–Wall–Ozawa (FWO), (c) Kissinger–Akahira–Sunose (KAS), (d) Coats–Redfern and (e) Kissinger. Graphs (a–d) correspond to different degrees of conversion ($\alpha = 0.15$ – 0.70) and heating rates (β), while graph (e) is based on T_{max} at different β . Note: β values are expressed in $^{\circ}C/min$. Calculations were performed using absolute temperature (K).

To present results of the application of Avrami’s model to the thermal degradation kinetics of the residues of the pruning of *P. americana*, Figure 4 shows the adjustment of the model to the TGA data in the range of ~ 252 – 362 $^{\circ}C$. This range was selected because it corresponds to the stage with the greatest degradation of the structural components of the biomass, including hemicellulose, cellulose, and some of the lignin. The graph shows a well-defined linear relation between $\ln[-\ln(1-\alpha)]$ and $\ln(\beta)$ for each temperature analyzed, and indicates an adequate correspondence of the model with the experimental data from pyrolysis for the distinct β values. This linear behavior suggests that, for the temperature

range evaluated, the kinetics of the process can be described by a consistent mechanism with no significant changes in the type of reaction as temperature varied.

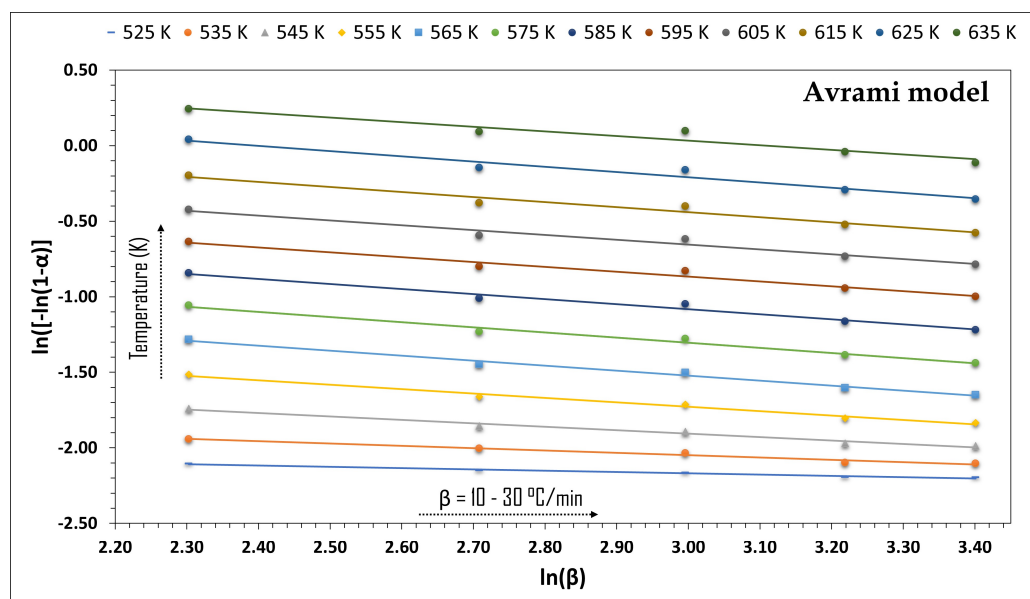


Figure 4. Avrami model fitting to TGA data of *P. americana* pruning residues.

The analysis of Figure 4 shows that as the temperature increased, the values of $\ln[-\ln(1 - \alpha)]$ also increased at the same heating rate. This result confirms a greater thermal conversion of the biomass. The similar slopes of the straight lines suggest that the reaction order, n , presented minimal variations, which indicate that the principal decomposition mechanism was conserved virtually constant across the temperature range evaluated. The increase in β , meanwhile, translates into a progressive reduction in $\ln[-\ln(1 - \alpha)]$ that manifests the influence of thermal residence time on the advance of the reaction. Taken together, these tendencies support the applicability of Avrami's model to describe the global kinetics of the thermal degradation of biomass, while the numerical values in Table 3 below permit a more detailed, quantitative interpretation of the kinetic behavior of the system that includes the temperatures analyzed, the linear adjustment slopes, the values for the reaction order, n , and the correlation coefficients obtained.

Table 3. Fractional order and fittings of the Avrami model for the thermal degradation of *P. americana*.

Temperature (°C/K)	Slope (m)	Reaction Order ($n = -m$)	Correlation Coefficient (R^2)
252/525	−0.0855	0.0855	0.9676
262/535	−0.1538	0.1538	0.9748
272/545	−0.2267	0.2267	0.9810
282/555	−0.2917	0.2917	0.9868
292/565	−0.3302	0.3302	0.9879
302/575	−0.3400	0.3400	0.9825
312/585	−0.3343	0.3343	0.9781
322/595	−0.3213	0.3213	0.9724
332/605	−0.3187	0.3187	0.9693
342/615	−0.3340	0.3340	0.9656
352/625	−0.3455	0.3455	0.9598
362/635	−0.3065	0.3065	0.9273
Average		0.2824	0.9711

The results of Avrami's model show a high adjustment level indicative of its suitability for describing the global kinetics of the thermal degradation of lignocellulosic biomass

(Table 3). The temperature range analyzed ($\sim 252\text{--}362\text{ }^{\circ}\text{C}$) covers the main stages of the decomposition of hemicellulose, cellulose, and lignin, and spans both the initial and advanced stages of the process. The parameter n shows a progressive increase with temperature, as the low values ($0.0855\text{--}0.2267$) in the lower interval reflect a gradual degradation of hemicellulose, while the maximum values (0.3455) in the upper interval indicate more complex kinetics associated with the simultaneous decomposition of residual cellulose, lignin, and intermediate products. This behavior, evidenced in the variability of n , is explained by the differentiated distribution of the activation energy and the heterogeneous nature of reactivity among the components of the biomass, as Cai et al. reported [51], supported by the usefulness of Avrami's model as an empirical tool to represent the global kinetics of a multistage process. These results suggest that degradation does not occur through one simple, elemental mechanism but, rather, is modulated by phenomena of diffusion, mass and heat transfer, and the superposition of thermochemical processes, including fragmentation of the structure, the release of intermediate volatiles, and the formation of solid residues [52]. Consequently, the kinetic analysis yields apparent parameters that describe this effective global behavior. The specific composition of the biomass, with high cellulose (46.8%) and hemicellulose (20.6%) content, moderate lignin content (14.5%), and high extractable fractions ($\sim 17\%$) (see Table 1), contributes to both the diversity of reactive routes and thermal heterogeneity, while also differentiating its kinetic behavior from that of other lignocellulosic biomasses, such as the wood of *Ceiba aesculifolia*, which shows greater uniformity due to its high cellulose content and lower proportions of hemicellulose, lignin, and extractables [12].

The consistency of the adjustments justifies using the average value of the fractional reaction order ($n = 0.2824$) when applying the Coats–Redfern method to estimate the kinetic parameters E_a and A (Table 4). Figure 3e presents the results of applying this model. The linear adjustments obtained reveal a high correlation that confirms its pertinence for describing the thermal degradation of biomass.

That figure also shows that as the degree of conversion increases ($\alpha = 0.15\text{--}0.70$), the curves shift progressively toward lower $1/T$ values. This indicates that the more advanced stages of the process occur at higher temperatures. Moreover, the grouping of the curves in the left region of the graph reflects a lower variation in the activation energy in these phases, while the slight differences in the slopes suggest that this parameter does not remain constant throughout conversion. This behavior is consistent with both the multicomponent nature of the biomass and the scaled degradation of hemicellulose, cellulose, and lignin.

The quantitative values derived from the models applied (Coats–Redfern, Friedman, FWO, KAS, and Kissinger) are shown in Table 4. Results include the values of E_a , the factor A , and the correlation coefficient (R^2) for the conversion interval $\alpha = 0.15\text{--}0.70$. For Kissinger's method, we report a single derived value of T_p for each heating rate.

The Friedman, FWO, and KAS iso-conversional methods all showed a progressive increase in E_a as the degree of conversion increased ($\alpha = 0.15\text{--}0.70$) with ranges of $174.6\text{--}302.3$, $167.4\text{--}225.9$, and $166.7\text{--}227.1$ kJ/mol, respectively. Kissinger's method provided a single value of 171.3 kJ/mol that corresponded to T_p . The factors A relate proportionally to E_a , as they reached values between 10^{12} and 10^{16} s $^{-1}$ with a maximum of 1.16×10^{22} s $^{-1}$, determined by Friedman's model for $\alpha = 0.70$. Every method displayed a robust adjustment with correlation coefficients (R^2) >0.97 .

Table 4. Kinetic parameters of *P. americana* branches determined using iso-conversional methods (Friedman, FWO, and KAS), the Kissinger method, and the Coats–Redfern integral method applied in this study at different heating rates ($\beta = 10\text{--}30\text{ }^{\circ}\text{C}/\text{min}$).

Method	Conversion, α	E_a (KJ mol ^{−1})	R^2	A (s ^{−1})
Coats–Redfern	0.15	177.8	0.9859	2.71×10^{14}
	0.20	165.2	0.9963	7.95×10^{12}
	0.25	163.8	0.9975	3.72×10^{12}
	0.30	166.8	0.9957	4.85×10^{12}
	0.35	171.4	0.9954	8.87×10^{12}
	0.40	177.2	0.9945	2.12×10^{13}
	0.45	183.2	0.9937	5.30×10^{13}
	0.50	190.7	0.9960	1.82×10^{14}
	0.55	198.4	0.9978	6.53×10^{14}
	0.60	200.6	0.9751	8.44×10^{14}
	0.65	207.8	0.9654	2.75×10^{15}
	0.70	221.0	0.9607	2.77×10^{16}
	Average	185.3	0.9878	2.70×10^{15}
Friedman	0.15	175.0	0.9925	3.60×10^{13}
	0.20	183.1	0.9931	1.10×10^{14}
	0.25	204.2	0.9837	5.14×10^{15}
	0.30	182.7	0.9895	3.49×10^{13}
	0.35	174.7	0.9824	4.21×10^{12}
	0.40	201.4	0.9856	5.93×10^{14}
	0.45	207.1	0.9844	1.20×10^{15}
	0.50	189.9	0.9806	3.13×10^{13}
	0.55	230.1	0.9837	5.46×10^{16}
	0.60	226.0	0.9844	2.73×10^{16}
	0.65	242.0	0.9774	2.33×10^{17}
	0.70	302.3	0.9907	1.16×10^{22}
	Average	209.9	0.9857	9.65×10^{20}
Flynn–Wall–Ozawa	0.15	177.0	0.9655	1.49×10^{15}
	0.20	167.4	0.9818	6.06×10^{13}
	0.25	167.7	0.9820	3.13×10^{13}
	0.30	170.1	0.9888	2.87×10^{13}
	0.35	175.9	0.9858	5.46×10^{13}
	0.40	181.1	0.9832	9.64×10^{13}
	0.45	187.4	0.9818	2.13×10^{14}
	0.50	194.4	0.9804	5.70×10^{14}
	0.55	201.4	0.9786	1.56×10^{15}
	0.60	207.8	0.9778	3.79×10^{15}
	0.65	215.6	0.9765	1.22×10^{16}
	0.70	226.0	0.9614	6.20×10^{16}
	Average	189.3	0.9786	6.84×10^{15}
Kissinger–Akahira–Sunose	0.15	177.1	0.9620	1.46×10^{15}
	0.20	166.7	0.9798	4.99×10^{13}
	0.25	166.9	0.9799	2.49×10^{13}
	0.30	169.3	0.9875	2.27×10^{13}
	0.35	175.1	0.9841	4.49×10^{13}
	0.40	180.5	0.9813	8.18×10^{13}
	0.45	187.0	0.9798	1.89×10^{14}
	0.50	194.3	0.9783	5.33×10^{14}
	0.55	201.6	0.9763	1.54×10^{15}
	0.60	208.1	0.9755	3.90×10^{15}
	0.65	216.2	0.9741	1.33×10^{16}
	0.70	227.1	0.9578	7.32×10^{16}
	Average	189.2	0.9764	7.86×10^{15}
Kissinger		171.3	0.9829	2.60×10^{12}

Regarding the pre-exponential factor, Friedman showed the greatest dispersion, with values between 4.21×10^{12} and $1.16 \times 10^{22} \text{ s}^{-1}$, while FWO and KAS presented tighter and more consistent intervals. Coats–Redfern achieved the best average fit ($R^2 \approx 0.9878$) and a mean A value lower than the iso-conversional methods, even though its variability was not the lowest. Kissinger, for its part, provided a single pair (E_a , A) associated with the maximum of the DTG signal, with A lower than the average of the differential and integral methods. The wide dispersion observed in A , particularly in Friedman, is consistent with the complexity of biomass pyrolysis and with what has been reported in the literature, where free-model methods tend to generate more dispersed values due to the superposition of multiple reactions [11].

The Coats–Redfern analysis generated E_a values of 163.8–221.0 kJ/mol and A values between the orders 10^{12} and 10^{16} s^{-1} , with R^2 of 0.9607–0.9978 (average 0.9878). The ascending tendency of E_a and A in the final stages reflects the transition of the more reactive components, like hemicellulose and cellulose, toward more stable fractions, such as lignin and condensed aromatic structures. This variation is consistent with the sequential decomposition of lignocellulosic pseudo-components: hemicellulose degrades at lower temperatures, cellulose in intermediate stages, and lignin at higher temperatures, due to differences in their molecular structure, crystallinity, and type of bonds, as has been documented in studies of pure components [47]. The progressive increase in E_a with α observed with the iso-conversional and Coats–Redfern methods confirms the multistage nature of the pyrolysis of biomass, characterized by the sequential degradation of more reactive fractions toward more recalcitrant components [19,53].

The proportional correlation between E_a and A evidences an effect of kinetic compensation consistent with transition state theory [20] and suggests related reaction mechanisms during the process. This behavior coincides with observations reported in experimental studies and reviews on biomass pyrolysis, where the linear relationship between A and E_a has been attributed to the kinetic compensation effect and the consistency of the predominant mechanisms in each reaction stage [11,44].

The values for the factor A are within the ranges reported for other lignocellulosic biomasses (with orders up to 10^{23} s^{-1}) [11]. Their increase toward higher degrees of conversion reflects greater energy demand and molecular dynamics in the final stages of degradation. The greater variability observed in the results of Friedman's method are interpreted as a manifestation of its sensitivity, which allowed us to identify in greater detail the stages of conversion that present significant kinetic changes, consistent with the multicomponent nature of the material [19]. In contrast, the FWO, KAS, and Coats–Redfern methods provided more uniform estimates that facilitate global, consolidated comparisons of the kinetic parameters. The single Kissinger value near the initial values of $\alpha = 0.15$ – 0.30 estimated with Coats–Redfern) confirms that this method reflects mainly E_a at point T_p and is coherent with the other approaches for purposes of global comparison.

The upward tendency of energy, E_a , seen observed herein relates to the scaled degradation of the lignocellulosic components of the prunings from avocado trees, which contain high percentages of cellulose (46.8%) and hemicellulose (20.6%), but a moderate contribution of lignin (14.4%) (Table 1). The kinetic parameters determined with the Friedman, FWO, KAS, Coats–Redfern, and Kissinger methods show a coherent evolution of E_a and the factor A that provide evidence of similar mechanisms during the process and reflect the transition from more reactive fractions (amorphous hemicellulose and cellulose) toward more recalcitrant components (lignin and condensed aromatic structures) [54]. The high volatile material content (83.8%) and low ash level (1.2%) reinforce the idea that the initial phase is dominated by the rapid release of organic compounds, followed by more complex stages where fragmentation and recombination reactions predominate to produce

carbonous residues. Overall, results show that the degradation dynamics of the branches is strongly conditioned by their chemical composition, and provide specific, quantitative information that is useful for analyzing and modeling pyrolytic processes of biomass in its natural state.

In addition to the multistage thermal behavior observed in the TGA and kinetic analyses, the physicochemical properties of the prunings of avocado trees support their potential for thermochemical conversion. The HHV (19.6 MJ/kg) lies in the range of woody biomasses of interest for energy studies and is particularly important in relation to the quality of the products of pyrolysis since high values favor obtaining liquid and gas fractions with good energy content and generating biochar that could be exploited as a solid fuel or an added-value input. However, the kinetic parameters determined (E_a up to ~ 302 kJ/mol; A up to 10^{22} s $^{-1}$) reveal a significant energy barrier that limits the thermal reactivity of this material. As a result, the heating potential identified does not translate automatically into an efficient conversion under conventional pyrolysis conditions. It is, therefore, essential to integrate kinetic criteria with the energy criteria when designing and optimizing processes in order to define strategies that will make it possible to overcome the material's thermal resistance and more effectively exploit its capacity to generate products with energy value.

The increasing tendency of E_a observed can be explained by the lignocellulosic composition of the material, where the scaled decomposition of hemicellulose, cellulose, and lignin generated a multistage behavior. In this sense, the functional characterization by FTIR supports the kinetic evolution since the signals associated with hemicellulose carbonyls (1740 cm $^{-1}$), polysaccharides (1245–1030 cm $^{-1}$), and aromatic lignin structures (160–1460 cm $^{-1}$) evidence an overlapping decomposition of these components. During the active phase (280–360 °C), when the largest increases of E_a were recorded, the spectrum confirms the transition from more reactive fractions toward more stable structures, a finding consistent with the growing participation of lignin. In advanced stages (>400 °C), the appearance of condensed aromatic signals (820 cm $^{-1}$) concurs with the formation of fixed carbon observed in the TGA and strengthens the relation between the thermal stability and chemical composition of the residue.

In previous studies under combustion conditions, the woody fraction of prunings of avocado trees presented E_a between 143.9 and 211.0 kJ/mol [55], values close to the ones obtained herein for pyrolysis (163.8–227.0 kJ/mol). This similarity indicates that the global thermal resistance of the material is comparable despite the distinct atmospheres. Pyrolysis, however, has the advantage of orienting the conversion process toward condensable, carbonous fractions of great interest for the field of energy. This underscores the importance of this focus for valorizing lignocellulosic residues.

In contrast, the studies of avocado seeds under pyrolytic conditions by Malagón-Romero et al. [6] reported E_a values by FWO and KAS of 24–226 kJ/mol, while the woody biomass of prunings evaluated in our work show higher, more consistent values (166–227 kJ/mol, FWO and KAS) that reflect greater thermal stability associated with their high lignocellulosic fraction. As was to be expected given the more homogeneous nature of the woody fraction compared to the heterogeneous composition of seeds, these results from a broad range of heating rates (10–30 °C/min) permit a more robust estimate of the kinetic parameters and stress the predictability of the thermal behavior of the branches for pyrolysis processes.

The kinetic results for the pyrolysis of branches of avocado wood present values above those reported for the woody biomasses of *Mangifera indica* (143.0–176.5 kJ/mol, Sharma & Mohanty [56]) and *Ceiba aesculifolia* (118–156 kJ/mol, Alvarado-Flores et al. [12]), suggesting that the thermal decomposition of the biomass of avocado prunings has higher

energy requirements. When comparing kinetic parameters with chemical composition, it is revealed that the trend in activation energies is not strictly governed by lignin content. Although *Mangifera indica* has the highest content of this polymer (23.8%), it does not exhibit the highest E_a values, suggesting the decisive influence of other components. The branches of *P. americana*, which have the highest extractive content (~17%), are distinguished by their kinetic complexity, evidenced by the very wide range of their pre-exponential factors (10^{12} – 10^{22} s^{−1}). This behavior is consistent with more diverse and complex decomposition pathways facilitated by these non-structural compounds. In contrast, the tighter ranges of *Mangifera indica* (10^{10} – 10^{13} s^{−1}) and *Ceiba aesculifolia* (10^4 – 10^{11} s^{−1}) reflect more uniform decomposition mechanisms, typical of the main lignocellulosic matrices. The lower E_a and A values in *Ceiba aesculifolia* are also consistent with its cellulose-dominated composition (66.2%) and low lignin content (10.8%). Taken together, these findings support the notion that the higher energy demand for the pyrolysis of *P. americana* is not dictated by a single biopolymer, but probably results from the synergistic interaction between its structural (intermediate lignin) and non-structural (high extractives) components, a perspective that constitutes a key contribution of this study.

Studies of the pyrolysis of agricultural residues and hardwoods report E_a values that fluctuate from approximately 74 to over 300 kJ/mol. In contrast, under combustion conditions some woody and fruit materials show even higher values (up to 370–420 kJ/mol). This reflects the influence of chemical composition, structure, and reaction atmosphere on thermal kinetics. The combination of these relatively high E_a values with high A factors tells us that the biomass of avocado prunings presents significant kinetic barriers, and suggests the importance of carefully adjusting operating parameters like temperature and residence time to achieve effective conversion. These results emphasize that the biomass of avocado prunings generates a complex dynamic reaction, one that requires stricter thermal conditions or prolonged residence times to achieve efficient conversion. However, they present more stable thermal behavior and more predictable kinetics, two especially important properties for biochar production.

The kinetic analysis of the branches of *P. americana* showed that thermal resistance increased with the degree of conversion. The Friedman, FWO, and KAS iso-conversional methods, together with the Kissinger and Coats–Redfern approaches, provided estimates of highly reliable kinetic parameters ($R^2 > 0.95$) that are consistent with the literature on lignocellulosic biomasses. This was especially true for the FWO, KAS, and Coats–Redfern methods. Activation energy (E_a) was determined between 163.8 and 302.3 kJ/mol, while the frequency factors (A) ranged from 10^{12} to 10^{22} s^{−1}, indicative of Arrhenius-type kinetic compensation. The non-linear, multiphase kinetics described by Avrami’s model (average order $n = 0.2824$; $R^2 = 0.9711$) reflected the simultaneity of the degradation mechanisms of cellulose, lignin, and intermediate products, whose n value was later used to calculate parameters using Coats–Redfern ($R^2 = 0.9878$). The coherence among the various models validates the solidity of our results, confirms the multistage character of the process, and places avocado biomass in a medium-to-high range of thermal stability.

3.2.3. Estimates of Thermodynamic Parameters

Table 5 displays the thermodynamic parameters of the thermal decomposition of *P. americana* (ΔH , ΔG , ΔS) obtained through the kinetic models applied at a heating rate of 10 °C/min. These values, calculated as a function of α , and their interpretation, are based on transition state theory [20], which establishes the formation of a high-energy, activated complex conditioned by E_a that makes it possible to representatively characterize the thermal and energy behavior of this biomass during pyrolysis.

Table 5. Thermodynamics parameters of *Persea americana* Mill at different heating rates.

Method	Conversion, α	ΔH (KJ/mol)	ΔG (KJ/mol)	ΔS (J/mol·K)
Coats–Redfern	0.15	173.3	179.6	−10.1
	0.20	160.6	179.9	−31.2
	0.25	159.1	180.0	−33.8
	0.30	162.0	179.9	−28.9
	0.35	166.5	179.8	−21.4
	0.40	172.3	179.6	−11.8
	0.45	178.2	179.4	−2.0
	0.50	185.6	179.2	10.4
	0.55	193.3	179.0	23.0
	0.60	195.5	178.9	26.7
	0.65	202.6	178.8	38.4
	0.70	215.8	178.5	60.2
	Average	180.4	179.4	1.6
Friedman	0.15	170.5	179.7	−14.7
	0.20	178.5	179.4	−1.4
	0.25	199.5	178.9	33.4
	0.30	178.0	179.4	−2.4
	0.35	169.8	179.7	−15.9
	0.40	196.5	178.9	28.4
	0.45	202.1	178.8	37.6
	0.50	184.8	179.2	9.0
	0.55	225.0	178.2	75.6
	0.60	220.8	178.3	68.6
	0.65	236.8	178.0	94.9
	0.70	297.0	176.8	194.1
	Average	205.0	178.8	42.3
Flynn–Wall–Ozawa	0.15	172.5	179.6	−11.4
	0.20	162.8	179.9	−27.6
	0.25	163.0	179.9	−27.2
	0.30	165.4	179.8	−23.3
	0.35	171.0	179.6	−13.9
	0.40	176.2	179.5	−5.3
	0.45	182.4	179.3	5.0
	0.50	189.4	179.1	16.5
	0.55	196.3	178.9	28.1
	0.60	202.6	178.8	38.5
	0.65	210.4	178.6	51.3
	0.70	220.7	178.3	68.4
	Average	184.4	179.3	8.3
Kissinger–Akahira–Sunose	0.15	172.6	179.6	−11.2
	0.20	162.1	179.9	−28.7
	0.25	162.2	179.9	−28.6
	0.30	164.5	179.8	−24.8
	0.35	170.3	179.6	−15.1
	0.40	175.6	179.5	−6.3
	0.45	182.0	179.3	4.3
	0.50	189.2	179.1	16.3
	0.55	196.5	178.9	28.3
	0.60	203.0	178.8	39.1
	0.65	211.1	178.6	52.5
	0.70	221.8	178.3	70.3
	Average	184.2	179.3	8.0
Kissinger		166.4	179.8	−21.5

Overall enthalpy values (ΔH) were high, indicating that the biomass requires considerable energy input to reach the activated state. As mentioned above, the combination of high ΔH values with high A factors reveals that this residue presents significant kinetic barriers. Hence, the design of pyrolysis processes to valorize energy requires careful control of the operating conditions, especially reaction temperature and residence time, to foster efficient, stable conversion. The behavior observed supports this residue's potential for applications that produce biocarbon, due to its relative resistance to thermal degradation and the possibility of modulating reactivity through adequate operating conditions.

The ΔH values obtained for *P. americana* (160.6–297.0 kJ/mol) place this material in the upper reaches of the range reported for other lignocellulosic biomasses, such as *Mangifera indica* (~150–180 kJ/mol, Sharma & Mohanty [56]) and *Ceiba aesculifolia* ($\approx$ 65–152 kJ/mol, Alvarado-Flores et al. [12]). The ΔH of prunings of avocado trees is relatively low in the initial stages of pyrolysis, but increases as conversion advances, suggesting that later phases of the process require greater energy inputs.

The positive, stable ΔG values (176.8–180.0 kJ/mol) confirm that pyrolysis of *P. americana* does not occur spontaneously, but requires a constant energy supply, as Van de Velden et al. [57] reported previously, plus the influence of resistant lignocellulosic components like lignin and carbonaceous materials [20,58]. These conditions foment the formation of stable biocarbon that has potential applications for carbon sequestration [58,59]. These ΔG values also exceed those recorded for sawdust from *Mangifera indica* (~151 kJ/mol, Sharma & Mohanty, [56]) and are slightly higher than those of *Ceiba aesculifolia* wood (~175 kJ/mol; Alvarado-Flores et al. [12]). These findings suggest greater thermodynamic stability attributable to structural differences. Such comparisons must, however, be interpreted in light of the specific experimental conditions employed (heating rate, reaction atmosphere), for they can significantly impact reported values.

Entropy (ΔS) showed marked variations, with values ranging from -33.8 to 194.0 J/mol·K. During the initial stages of conversion ($\alpha = 0.15$ – 0.40), we observed negative ΔS values, typical of a more ordered state of the system and lower reactivity. As pyrolysis advanced, ΔS acquired positive values, reaching a maximum of ~ 194 J/mol·K at $\alpha \approx 0.70$, indicative of an increased structural disorder and a higher reaction velocity associated with the fragmentation of hemicellulose, cellulose, and lignin [4].

For biomasses like *Mangifera indica*, negative ΔS values were determined for the initial stages, but turned positive in the intermediate intervals (-34.3 to $+34.0$ J/mol·K) [56], though a study of *Ceiba aesculifolia* generated only negative ΔS values (-34.8 to -185.6 J/mol·K) [12]. This was also the case of olive and palm leaves and wheat straw, which generated negative ΔS values (-183 to -192 J/mol·K) [19].

In conjunction with the relatively high ΔH and ΔG values obtained for the branches of *P. americana*, which are at the upper end of the ranges reported for *Mangifera indica* and *Ceiba aesculifolia*, the evolution of ΔS toward positive values in intermediate and advanced stages reinforces the idea of a thermal conversion process that requires greater energy inputs and exhibits a progressive increase in structural disorder. This response could be associated with the combination of an intermediate lignin content and a high proportion of extractives, factors that may favor more diverse decomposition processes and thermodynamic behavior different from that observed in biomasses of more conventional composition. Considering the evolution of ΔS together with ΔH and ΔG is essential for understanding the thermal conversion of this biomass and for improving the kinetic and thermodynamic modeling approaches applied to its pyrolysis.

The pyrolysis of lignocellulosic biomass presents marked variation in thermodynamic and kinetic parameters that depends on the chemical composition, heating rate, degree of conversion, and calculation methodology applied [4]. This heterogeneity underscores the need to evaluate each type of biomass individually in relation to its thermochemical nature in order to optimize processes designed to obtain products with energy or chemical value [4,9,60].

The thermodynamic parameters obtained support the tendencies observed in the kinetic analysis and confirm that pyrolysis of avocado prunings is a non-spontaneous, endothermic process. Activation enthalpy (ΔH) ranged from 160.6 to 297.0 kJ/mol and increased with the degree of conversion (α). This indicates greater energy demand in advanced stages of the process. The fact that Gibbs free energy (ΔG) remained around

170 kJ/mol identifies the process as non-spontaneous. Entropy (ΔS), in turn, presented negative values for $\alpha = 0.15$ – 0.40 but positive ones from $\alpha = 0.45$, with a total range of -158 to 194 J/mol·K. These results reveal a transition toward more disordered states as degradation advanced.

The thermodynamic parameters determined for *P. americana* branches show relatively high values of ΔH and ΔG compared to similar biomass, reflecting the thermal resistance of this waste and its potential to promote conversion to biochar. These values indicate that pyrolysis requires a controlled energy input, allowing temperature profiles and residence time to be adjusted to optimize the formation of a stable carbonaceous solid fraction, minimizing the volatilization of less resistant components. The positive progression of ΔS with the degree of conversion suggests a structural transition towards more disordered states, associated with the gradual release of volatiles and the stabilization of aromatic structures in the biochar. Taken together, these findings reinforce the importance of kinetic and thermodynamic parameters in designing efficient pyrolysis strategies and maximizing recalcitrance and carbon retention in biochar [57,59].

Since this study focuses on the valorization of pruning residues, the kinetic parameters obtained reflect an apparent behavior inherent to realistic processing conditions, where heat and mass transfer effects are significant. This effective kinetics provides a highly applicable foundation for reactor-scale modeling and process optimization. Consequently, the results deliver a robust and practical characterization that directly supports the experimental scaling of pyrolysis, the evaluation of value-added products, and the development of predictive tools for designing more efficient thermochemical valorization pathways for lignocellulosic residues.

4. Conclusions

The thermal decomposition of *Persea americana* pruning residues showed that the maximum degradation rate is concentrated within a lower (315 – 360 °C) and narrower interval compared to the typical ranges reported for isolated components (cellulose ~ 345 °C, lignin ~ 400 °C). This evidence indicates a synergistic and accelerated decomposition of the structural components. This overlap suggests that the pyrolysis of this biomass is dominated by interactive reactions that concentrate the greatest mass loss within a reduced thermal window, favoring an intense and early release of volatiles.

Kinetic analysis demonstrated that the combined Avrami–Coats–Redfern approach is the most suitable for describing this process. The Avrami model yielded a low reaction order ($n \approx 0.28$), and applying this value in the Coats–Redfern model provided the best fit ($R^2 \approx 0.9878$) and the narrowest range of pre-exponential factors ($A = 10^{12}$ – 10^{16} s $^{-1}$), indicating greater parametric consistency. The activation energies (E_a between 185 and 210 kJ/mol) lie at the upper end of the range reported for other lignocellulosic biomasses, suggesting a higher inherent thermal stability for this biomass.

The estimated thermodynamic parameters ($\Delta H = 166$ – 206 kJ/mol; $\Delta G \approx 179$ kJ/mol), positioned at the upper range of those reported for other woody biomasses, indicate a thermal conversion process that requires a relatively high energy input. This trend suggests that the structure of this biomass exhibits moderately high thermal stability against degradation. The observed entropy increase (ΔS up to 194 J/mol·K), while consistent with that documented for comparable woods, reflects the transition toward more disordered activated states without revealing atypical behavior.

This kinetic–thermodynamic profile explains why slow to intermediate pyrolysis regimes are optimal for this biomass: they allow overcoming its high energy barrier and controlling the intense release of volatiles, thereby maximizing biochar yield. The study establishes a specific and comparative reference framework for *P. americana*, validating the

effectiveness of the Avrami–Coats–Redfern model and providing distinctive parameters for process design.

A limitation of the study is the absence of identification and quantification of the extractive fractions of *P. americana*, which prevented the evaluation of their potential contribution to certain FT-IR bands (such as the one observed at $\approx 2860\text{ cm}^{-1}$) and a more precise determination of their influence on the observed thermochemical behavior. Given that the composition of extractives can modify both certain spectroscopic responses and aspects of thermal decomposition, it is considered pertinent for future work to incorporate their characterization to elucidate their role in the thermal evolution of this biomass.

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